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(21)Application number : 2002-126295 (71)Applicant : HITACHI POWDERED
METALS CO LTD
NISSAN MOTOR CO LTD

(22)Date of filing : 26.04.2002 (72)Inventor : SHIROHIGE MINORU
IIDA JUNICHI
ITO HITOSHI
KATAMURA JUNJI
KAWAI MIKIO

(54) GRAPHITE-BASED HYDROGEN-OCCLUDING MATERIAL AND METHOD FOR PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To achieve a graphite-based hydrogen-occluding material which can effectively occlude hydrogen, is lightweight, can be repeatedly used and easily produced, and to achieve a method for producing the same.

SOLUTION: The graphite-based hydrogen-occluding material comprises a graphite-based material which occludes and releases hydrogen, wherein the graphite-based material is at least ground and activated to have a specific surface area of 400 m²/g or more and a volume of pores having a radius of 5 nm or less of 0.3 cm³/g or more.

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CLAIMS

[Claim(s)]

[Claim 1] The graphite system hydrogen absorption ingredient with which activation is carried out and this graphite system ingredient is characterized for hydrogen by grinding and the volume of pore with a radius of 5nm or less having become [specific surface area] more than 400m² / g 0.3cm³ / more than g at least in occlusion and the graphite system ingredient to emit.

[Claim 2] 1360cm⁻¹ resulting from the graphite which is called D band from which said graphite system ingredient is obtained by laser-Raman-spectroscopy analysis and which was made amorphous Graphite system hydrogen absorption ingredient according to claim 1 whose R value which shows a peak height ratio (I1360/I1575) with the spectral intensity (I1575) of the 1575cm⁻¹ neighborhood resulting from the crystalline substance carbon of neighboring spectral intensity (I1360) and the graphite called G band is 0.70 or more.

[Claim 3] The graphite system hydrogen absorption ingredient according to claim 1 or 2 which contains any one or more sorts of elements of Pt, Pd, nickel, K, Li, Ti, V, Cr, Mn, Fe, Co, Zr, and Nb into said graphite system ingredient.

[Claim 4] The manufacture approach of the graphite system hydrogen absorption ingredient characterized by producing to a thing according to claim 1 or 2 by carrying out activation processing as the second process after carrying out grinding processing as the first process and making magnitude of the microcrystal of a graphite small using any one or more sorts of raw material graphites of a natural graphite, an artificial graphite, and a mesophase pitch system graphite.

[Claim 5] The manufacture approach of a graphite system hydrogen absorption ingredient according to claim 4 that the magnitude of the microcrystal of the field (110) of the graphite before said grinding is [the magnitude of the microcrystal of 25nm or more and a field (002)] a thing 20nm or more.

[Claim 6] The manufacture approach of a graphite system hydrogen absorption ingredient given in claims 4 and 5 from which the magnitude of the microcrystal of the field (110) of the graphite after said grinding is 1nm or more and the range whose magnitude of the microcrystal of a field (002) is 1-70nm.

[Claim 7] The manufacture approach of a graphite system hydrogen absorption ingredient given in claims 4, 5, and 6 which carry out content processing of any one or more sorts of elements of Pt, Pd, nickel, K, Li, Ti, V, Cr, Mn, Fe, Co, Zr, and Nb as the third process after [said] carrying out activation processing.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the hydrogen absorption ingredient and its manufacture approach of a graphite system. In addition, in this specification, nickel, Pt, Pd, K, Li, etc. are the symbols of element.

[0002] While development competition of a polymer electrolyte fuel cell is developed actively, cost is low, since it is utilization, especially the thing that is having the mount to the device for transportation inquired is lightweight, an occlusion consistency is high, and restoration of hydrogen and development of the hydrogen preservation using a hydrogen absorption ingredient with a quick emission rate are desired. As an approach of mounting current and hydrogen to the device for transportation, four kinds of approaches, high pressure gas, liquid hydrogen, a hydrogen storing metal alloy, and a carbon system ingredient, are proposed. Here, carrying high pressure gas in a vehicle is put in practical use by natural gas (methane) automobile, and it is compressed to 200 atmospheric pressures and stored in a bomb. Therefore, essentially making to use a hydrogen bomb for a fuel cell powered vehicle into 350 atmospheric pressure, in order to increase a hydrogen quantity to be stored satisfactory, and increasing a fill is examined. However, in order that a bomb may bear high pressure, it is made heavy-gage and has the problem that weight increases. Next, by transportation storage by liquid hydrogen, liquefaction hydrogen can be manufactured by making it low temperature from the boiling point (-253 degrees C) of hydrogen. Since the volume is about 1/800 compared with a gas, liquefaction hydrogen is the storage condition which was excellent in hydrogen. However, the evaporation (boil off) in which the heat of vaporization of hydrogen originates in a small thing, the point of requiring the container with which ultra low temperature is borne, etc. serve as a technical problem. On the other hand, as transportation storage by the hydrogen storing metal alloy, it is LaNi₅ of the rare earth system alloy currently used also for nickel-hydrogen cell. It is typical. The hydrogen storage capacity of this ingredient is about 1.4wt%. Moreover, it turns out that the solid-solution phase which has body center cube (BCC) structure in the alloy based on Ti and V is excellent in hydrogen absorption nature, and examination is advanced recently. On the other hand, research of the hydrogen absorption using a carbon system ingredient is done briskly in recent years. Although it is activated carbon, intercalated graphite, a carbon nanotube (CNT), a graphite nano fiber (GNF), and fullerene and has the technical problem as a carbon system ingredient in occlusion and the emission characteristic, a manufacturing cost, mass-production nature, yield in ordinary temperature, etc., further examination is advanced that the technical problem should be conquered. Specifically, it is as follows.

[0003] 4 which hydrogen absorption method using CNT attracted attention most among carbon system ingredients, and was superior to occlusion ability of hydrogen storing metal alloy - 10wt% -- the report of occlusion ability achievement [before and after] is also made. It is cylindrical and Monolayer CNT takes the structure whose diameters in which the graphene sheet of one sheet which the carbon atom arranged in the shape of a hex steel eye was round are a number - 10nm of numbers and which they consisted bundle-like (the shape of a bundle) of in many cases, between the interior of a tube, or a tube, strong physical potential acts and it is suppose that a lot of hydrogen content

children physisorb it there. Since multilayer CNT is that to which the graphene sheet lapped with concentric circular at equal intervals at the multilayer and a tube wall is a multilayer, the rate of a surface carbon atom of contacting a hydrogen content child decreases, but if hydrogen advances into graphene sheet spacing, it is supposed that a high hydrogen absorption function is expectable. moreover, a multilayer -- what has the high amount of preferred orientation is compounded by development of the synthesis method of CNT, consequently the report of a high hydrogen storage capacity is made. In addition, the technique of carrying out occlusion of the hydrogen to the carbon material which has pores, such as CNT, GNF, and activated carbon, is proposed by JP,2001-220101,A. However, generally, high hydrogen absorption can be attained at the low temperature near liquid nitrogen, and the occlusion ability in ordinary temperature has many 0.2 - 0.4wt% and low technical problems, such as improvement in cost reduction large for utilization, and production capacity, at nano CHUPU. In JP,2001-302224,A, the proposal to which grind a graphite mechanically in a hydrogen ambient atmosphere, and hydrogen is made to store in the graphite by which nano structuring was carried out is also made, and 7.4wt% hydrogen desorption is checked. It is characterized by storing hydrogen without covalent bond and covalent bond in a graphite particle by grinding a graphite in a hydrogen ambient atmosphere, and big occlusion nature is checked. This technique is explained by reference (carbon TANSO 2001 "No.200" pp 261-268) in full detail. When an example is given, the amount of hydrogen inside "nano structuring graphite increases remarkably with the increment in the milling processing time, i.e., development of defect structure, and it turns out that the amount of hydrogen of 80 hours after reaches also to 7.4wt(s)%. The specific surface area after milling processing of 80 hours is the order of only 10m²/g, and there are very few amounts of physical adsorption on the front face of a sample. Moreover, the temperature-programmed-desorption spectrum of the hydrogen content child of the mass number 2 showed 2 peaks which start in about 600K and 950K. Interesting analyses, such as ", are made. However, on the occasion of actual use, cycle nature (use of a repeat) needs low temperature-ization of hydrogen desorption temperature, and to be secured. The hydrogen absorption nature in a hydrogen ambient atmosphere is supposed that the dangling bond and structure defect which are produced by grinding have driving force, and it is reported that they are the hydrogen which has combined the hydrogen's existence location with the dangling bond of a graphite from the neutron diffraction experiment, and hydrogen to which another is located between graphite layers. Therefore, since it is in the condition made amorphous by the microcrystal of a graphite being small even if hydrogen hardly enters (0.2wt%) and grinds in a hydrogen ambient atmosphere again in pressurization, when putting hydrogen into the ingredient to which heated once and hydrogen was made to emit, it is a problem that the occlusion of hydrogen is hardly accepted. Therefore, it is a problem that emission temperature's being high and use of a repeat cannot be performed in grinding in a hydrogen ambient atmosphere.

[0004]

[Problem(s) to be Solved by the Invention] Although the above carbon system ingredients show hydrogen absorption ability higher than a hydrogen storage material depending on storage / emission conditions, there are many problems -- emission temperature is not high, cannot perform use of a repeat on an occlusion mechanism, or mass production method is impossible on a process. Then, occlusion of this invention can be carried out

efficiently, and it is lightweight, can use a lot of hydrogen repeatedly, and also aims production at offering an easy graphite system hydrogen absorption ingredient and its manufacture approach.

[0005]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, as a result of repeating research wholeheartedly using the graphite with easy acquisition and manufacture as a raw material from a viewpoint of how the structure of a graphite is used, or how to use the surface activity of a graphite, using the crystalline good graphite, this invention persons are combining grinding and activation, and resulted that high hydrogen absorption nature could be attained in a header and invention. Namely, in occlusion and the graphite system ingredient to emit, at least, activation is carried out and, as for the graphite system hydrogen absorption ingredient of invention, this graphite system ingredient is characterized for hydrogen by grinding and the volume of pore with a radius of 5nm or less having become [specific surface area] more than $400\text{m}^2/\text{g}$ 0.3cm^3 / more than g.

[0006] The above invention can be specified more as a detail like claims 2-7.

- Invention of claim 2 is 1360cm^{-1} resulting from the graphite which is called D band which is what specified said graphite system hydrogen absorption ingredient from the crystal description, and is obtained by laser-Raman-spectroscopy analysis and which was made amorphous. The R value which shows a peak height ratio (I_{1360}/I_{1575}) with the spectral intensity (I_{1575}) of the 1575cm^{-1} neighborhood resulting from the crystalline substance carbon of neighboring spectral intensity (I_{1360}) and the graphite called G band is 0.70 or more.

- Invention of claims 3 and 7 is that said graphite system ingredient contains any one or more sorts of Pt, Pd, nickel, K, Li, Ti, V, Cr, Mn, Fe, Co, Zr, and the Nb, and specifies that the hydrogen storage capacity of per a unit weight (mass) can be increased more.

- Invention of claim 4 is what caught the above graphite system hydrogen absorption ingredient from the manufacture approach, and after it carries out grinding processing as the first process and it makes magnitude of the microcrystal of a graphite small using any one or more sorts of raw material graphites of a natural graphite, an artificial graphite, and a mesophase pitch system graphite, it is characterized by producing by carrying out activation processing as the second process.

- Invention of claims 5 and 6 is what specified the details of said manufacture approach, and the crystalline high thing of a graphite system raw material is good. The magnitude of the microcrystal of 25nm or more and a field (002) uses [the magnitude of the microcrystal of the field (110) of the graphite before grinding] a thing 20nm or more, In grinding processing, it becomes indispensable that the magnitude of the microcrystal of the field (110) of the graphite after grinding makes it 1nm or more and the range whose magnitude of the microcrystal of a field (002) is 1-70nm.

[0007]

[Embodiment of the Invention] Hereafter, the graphite system hydrogen absorption ingredient and the manufacture approach of invention are explained. After the graphite system hydrogen absorption ingredient of invention makes magnitude of the microcrystal of a graphite small by grinding processing as the first process using a crystalline high graphite, it is the first description as the second process to have adjusted pore, specific surface area, etc. of an ingredient to the optimal gestalt by activation processing. First, it

is required as a view of a graphite system ingredient with many hydrogen storage capacities to invent the sites (between layers, pore, etc.) which carry out occlusion of the hydrogen in a graphite. When this invention persons repeat a trial, even if they do activation processing of the crystalline high graphite which omits grinding processing, specific surface area does not increase from this point, and most development of pore structure is not seen, After making microcrystal of a graphite adjustment of a graphite system hydrogen absorption ingredient with a high specific surface area small (7nm or less) by grinding processing as the first process and lowering the degree of graphitization on the front face of a graphite, the corroboration that it is most desirable performing activation processing as the second process was obtained. That is, that specific surface area is raised in this invention using a crystalline high raw material graphite, and the graphite system hydrogen absorption ingredient which has the pore size and the crystal structure to which it is easy to stick physically [a hydrogen content child or a hydrogen atom] and chemically as a site where an activity, i.e., hydrogen, is easy to carry out occlusion of between pore structure and a layer more effectively is offered. The hydrogen adsorption property of the active spot produced as chemical potential of hydrogen absorption in the dangling bond produced in the grinding process of a graphite, a lattice defect, etc. and the graphite surface functional group produced in activation processing is used. Specifically, the physical adsorption site as for which the activity pore structure produced by grinding of a graphite progresses as a microstructure part (micropore) further in activation processing, and hydrogen tends to carry out occlusion is formed by combining activation processing on predetermined conditions as grinding processing and the second process as the first process.

[0008] Here, as a raw material graphite, i.e., a graphite before grinding, a crystalline high thing is desirable, and the magnitude of the microcrystal of a field (110) is that the magnitude of the microcrystal of 25nm or more and a field (002) uses a thing 20nm or more. As grinding effectiveness, especially this can expect the improvement in the volume of the pore in a grinding processing process, can also shorten grinding time amount, and is a desirable mode. Graphites with which crystallinity progressed, such as an artificial graphite which calcinates and manufactures natural graphites, such as a scale-like graphite, flaky graphite, and an earthy graphite, corks, etc. as a concrete raw material graphite, and a mesophase pitch system graphite which calcinates a mesophase pitch as a raw material, are suitable.

[0009] The range optimal as hydrogen absorption exists in grinding processing, and the range is that the magnitude of the microcrystal of the field (110) of the graphite after grinding stores in 1nm or more and the range whose magnitude of the microcrystal of a field (002) is 1-70nm. For a crystalline high raw material graphite, this is for the magnitude of the microcrystal of a field (110) and (002) a field to cause reduction of specific surface area and pore volume conversely by the condensation of a nano particle and microcrystal etc. in grinding of long duration which is set to 1nm or less, and for the hydrogen storage engine performance to fall, although the magnitude of microcrystal decreases by grinding and specific surface area and pore volume increase in connection with it. In addition, in grinding processing, a ball mill, a vibration mill, a planet ball mill, a jet mill, etc. are suitable as a grinder. Moreover, as for a grinding ambient atmosphere, atmospheric air, an argon, nitrogen, hydrogen, vacuum grinding, etc. are applied.

[0010] In activation processing, specific surface area is made high to a predetermined

value, being able to apply steam activation, carbon gas activation, oxygen activation, and a chemical activation method, and leaving the crystallinity of the graphite ingredient after grinding. Even if this is a crystalline high raw material graphite like future, after grinding it on the conditions to which specific surface area does not go up only by activation processing of the second process, magnitude of microcrystal is moderately made small by grinding which is the first process, and amorphous-ization on the front face of a graphite becomes moderate, it is performing activation processing of the second process, and is because adjustment of a graphite system ingredient with a high specific surface area which was most excellent as an object for hydrogen adsorption enables.

[0011] The detail of activation processing is as follows. At steam activation, a graphite sample is advanced by steam's existence-ization and a reaction is advanced at about 750 degrees C. At carbon gas activation, a reaction is advanced at about 850 degrees C by carbon gas's existence-ization. By the chemical activation method, the graphite after grinding infiltrates an activation chemical equally, it heats in an inert gas ambient atmosphere, and detailed pore is formed by dehydration and oxidation reaction of a chemical. In the case of the KOH activation which used the potassium hydroxide also in chemical activation, it is being 700 degrees C and making KOH react for 1 hour in **** for the amounts of 4 times of the amount of graphites, and inert gas. After activation processing, although a scaling object is formed in a graphite front face, the structure is a hydroxyl group, a carboxyl group, a carbonyl group, etc. The vacuum heat deairing of these is carried out on the occasion of hydrogen absorption (trial). Thus, a graphite discovers surface activity and the physical and chemical adsorption property of after [activation] of hydrogen improves.

[0012] The second description of invention is that the R value from which the volume of pore with a radius of 5nm or less serves as [specific surface area] more than 0.3cm³/g and a crystalline scale more than 400m²/g is formed or more in 0.70 as a graphite system hydrogen absorption ingredient obtained as mentioned above. Although a hydrogen absorption property is in such a good inclination that specific surface area is large here, in order that a hydrogen storage capacity is increased, and it may be stabilized, and occlusion of the hydrogen may be carried out or it may emit it that specific surface area is more than 400m²/g and that the volume of pore with a radius of 5nm or less is more than 0.3cm³/g, it becomes indispensable from hydrogen absorption and the emission characteristic.

[0013] From laser-Raman-spectroscopy analysis, the R value used as a crystalline scale is a value computed from the intensity ratio ($R = I_{1360} / I_{1575}$) of the Raman band of the 1575cm⁻¹ neighborhood and the 1360cm⁻¹ neighborhood, and usually makes this R value the parameter of structure. For example, it is ** resulting from the band of 1355-1360cm⁻¹ besides the band shifted to 1575-1600cm⁻¹ by what has low crystallinity to one Raman band existing in the 1575cm⁻¹ neighborhood in a natural graphite originating in the 2-dimensional hexagonal lattice which forms a carbon reticulated flat surface, the symmetric property of a hexagonal lattice having fallen according to the structure defect, or the band of 1360cm⁻¹ having been lost. Therefore, what has the stronger band strength of the 1360cm⁻¹ neighborhood will have more structure of a carbon defect. Moreover, there is not necessarily no laser Raman spectrometry in a correlation with the magnitude of the microcrystal for which it asked from the X diffraction from which the information on several 10nm depth direction is acquired from the surface of an ingredient, and the

crystal structure of bulk is acquired. For example, although the crystallinity which what ground the crystalline high graphite evaluates by the case where a lattice defect and amorphous-ization advance from a fine-particles surface, according to an X diffraction is high, it has that the crystallinity evaluated by laser Raman spectrometry is low. For this reason, it is important for coincidence to analyze both as specification of a hydrogen absorption ingredient. Especially a lamellar crystal like a graphite is still more so, when there is a possibility that the crack and lattice defect which are produced from grinding may occur from the surface part of a graphite, and amorphous-ization may also advance to coincidence. From such a point, this invention persons judged the surface state of the graphite sample after grinding and activation after grinding that grasping in crystal structure is effective in preparation of hydrogen absorption material again, made various ingredients as an experiment, and verified the optimal R value to which the occlusion of the hydrogen is easy to be carried out in a tentative way. That is, this invention is making or more into 0.70 the R value which serves as a crystalline scale from that test result as a graphite system hydrogen absorption ingredient obtained on the above-mentioned grinding processing and activation processing conditions, and enables increase of the amount of occlusion that it is easy to carry out occlusion of the hydrogen.

[0014] The third description of invention is containing any one or more sorts of Pt, Pd, nickel, K, and the Li as the above graphite system hydrogen absorption ingredient. The effective thing was checked, when it was able to be increased to about 1.1 to 1.8 times by this point compared with the time of a hydrogen storage capacity not containing by containing these, and a hydrogen storage capacity was increased or it improved a hydrogen desorption property from a trial. Moreover, any one or more sorts of Ti, V, Cr, Mn, Fe, Co, Zr, and the Nb may be contained. Because, since atomic hydrogen is smaller than a hydrogen content child condition, the hydrogen absorption to carbon is because the better hydrogen absorption engine performance is obtained, and the element of Ti, V, Zr, and Nb which are generally the principal component of a hydrogen storing metal alloy and the metallic elements belonging to the lanthanoids of the atomic numbers 57-71, or these alloys are also effective as a metal which decomposes a hydrogen content child to atomic hydrogen. Although the affinity with hydrogen becomes weaker rather than Ti, V, Zr, and Nb, it is also effective to add the alloy which mixed Cr, Mn, Fe, and Co with the bottom of the above-mentioned metal existence. As an approach of making the graphite ingredient after grinding and activation processing containing Pt, Pd, nickel, K, Li, etc., technique, such as a sinking-in method, self-possessed method, and ion-exchange method, grinding, and mixed vacuum firing, is applicable. Next, an example is given and the above invention is clarified further.

[0015]

[Example] (Examples 1-4) This example is what investigated the graphite system hydrogen absorption ingredient used as the candidate for invention, and its effectiveness, and is an example when changing grinding and activation processing conditions, using a natural graphite as a raw material graphite.

<preparation of a sample> -- in this example, each sample in Table 1 (examples 1-4) was produced by using the scale-like graphite of 18 micrometers of mean diameters, and developing a meso hole and micropore by activation processing (above-mentioned steam activation or KOH activation) as a natural graphite, using a ball mill, after [suitable] carrying out time amount grinding. In Table 1, the example 1 of a comparison is the

sample which did not grind said scale-like graphite but was produced by activation processing. The example 2 of a comparison is the sample which omitted the activation processing after grinding. The measuring method of pore structure, an R value, X-ray diffraction analysis, and a hydrogen storage capacity and a burst size is as follows.

<measurement of pore structure> -- analysis was asked for measurement of the specific surface area [m^2 / g] of each sample from the BET equation by Brunauer-Emmett-Teller using the nitrogen adsorption process (conformity specification: ISO 9277). Measurement of pore distribution uses the capillary condensation in liquid nitrogen temperature, and the formula of Kelvin serves as a foundation. Adsorption equilibrium pressure is changed over the large range, and pore distribution can be found if adsorption isotherm is drawn and analyzed. The analysis approach of this pore distribution was analyzed by the approach (BJH law) proposed by Barrett, Joyner, and Halenda. The relation between pore size and pore volume has been grasped, and it integrated and asked for the pore volume from 0.85nm of pore radii to 5nm, and considered as the pore volume of 5nm or less of pore radii. In addition, the measuring device of specific surface area and pore system distribution (pore size and pore volume) used ASAP2010 made from microphone ROMETORIKKUSU.

a <R value> -- 1360 cm^{-1} resulting from the graphite which this R value measures the Raman spectrum of each sample (sample after activation) with micro Raman spectrograph, and is called D band and which was made amorphous With neighboring spectral intensity (I1360) It computed, the relative intensity ratio (I1360/I1575), i.e., the peak height ratio, with spectral intensity (I1575) of the 1575 cm^{-1} neighborhood resulting from the crystalline substance carbon of the graphite called G band, and used for evaluation of a degree of graphitization. this Raman analysis equipment -- the Jasco make -- NR-1800 were used.

<X-ray diffraction analysis> -- it asked for the magnitude (L_a , L_c) of the microcrystal of each sample (each sample grinding before and after grinding) from Gakushin method using X-ray diffractometer. The measuring device used MXP18VAHF by Mac Saisensha.

[0016] <sample evaluation> -- each sample of an example and the example of a comparison performed measurement of a hydrogen storage capacity and the amount of hydrogen desorption with the test method according to JIS 7201 and 7203. In this measurement, after having put into sample tubing after weighing each sample precisely, and carrying out evacuation, hydrogen pressure was raised to 12Mpa and the hydrogen storage capacity [wt%] was measured. Moreover, next, it returned to ordinary temperature and the amount of hydrogen desorption was checked. The cycle property measured the aforementioned occlusion and the hydrogen storage capacity [wt%] after repeating emission 5 times. The above sample configuration and its evaluation result were shown in Table 1. Thing, **, and x of invention of the invention range are [O] out of range during evaluation.

[0017]

[Table 1]

[0018] In Table 1, it is an example which does not perform grinding processing, specific surface area does not become large after activation processing, and the thing of the example 1 of a comparison has too small pore volume with a radius of 5nm or less, and there are few hydrogen storage capacities. An R value becomes small and the thing of the example 2 of a comparison has few hydrogen storage capacities, although it is the example which does not perform activation processing to an example 1 or 2, and specific surface area becomes large to the invention range only in case of grinding. On the other hand, examples 1-5 are examples of invention which ground and processed [activation]. Among these, the thing of examples 1 and 2 is the example which performed activation processing by steam activation and KOH activation, both specific surface area, an R value, and pore volume with a radius of 5nm or less increase [the direction of KOH activation] as activation processing, and hydrogen absorption ability and its cycle property improve. Although it is what changed grinding time amount to the example 2 and specific surface area, an R value, pore volume with a radius of 5nm or less, the hydrogen absorption ability accompanying it, and a cycle property are somewhat changed by grinding time amount, as for the thing of examples 3 and 4, it turns out that it can improve several steps compared with the example 1 of a comparison, or the thing of 2. After grinding a graphite, while performing activation processing and carrying out

specific surface area as a graphite system hydrogen absorption ingredient by these more than 400m²/g, it becomes the most desirable mode that the R value from which the volume of pore with a radius of 5nm or less serves as more than 0.3cm³/g and a crystalline scale carries out to 0.70 or more.

[0019] (Examples 5-7) This example is an example which investigated the effect by the magnitude of a raw material graphite and its microcrystal, and the magnitude of the microcrystal after grinding.

<preparation of a sample> -- as this raw material graphite, although the example 3 of a comparison and an example 5 are artificial graphites, the example 3 of a comparison is a bad crystalline raw material with small microcrystal, and an example 5 is a raw material with larger microcrystal than it. Examples 6 and 7 and the example 4 of a comparison are a mesophase pitch system graphite (example 6) with large microcrystal, and a scale-like graphite (an example 7 and example 4 of a comparison). Each sample raw material carried out grinding processing using the ball mill. In this grinding, the example 3 of a comparison and the example 5 pulverized the example 4 of a comparison for examples 6 and 7 for about 1.5 hours for about 96 hours for about 3 hours. Then, each sample developed a meso hole and micropore by activation processing (the above-mentioned KOH activation), and was adjusted as each sample in Table 2 (examples 5-7, examples 3 and 4 of a comparison). In addition, it is the same as the measuring method of pore structure, an R value, X-ray diffraction analysis, and a hydrogen storage capacity and a burst size, and the case of the example described above about sample evaluation. The above sample configuration and its evaluation result were shown in Table 2. Thing, **, and x of invention of the invention range are [O] out of range during evaluation.

[0020]

[Table 2]

[0021] In Table 2, the magnitude of the microcrystal of a raw material graphite becomes important from the comparison of the example 3 of a comparison, and an example 5, in order that both the magnitude of the microcrystal after grinding may improve a hydrogen storage capacity from the comparison of the example 4 of a comparison, and an example 7. Moreover, it turns out that the R value of a cycle property [a hydrogen storage capacity and] from which the specific surface area after activation serves as a scale of the crystallinity [volume / of pore with a radius of 5nm or less] of more than 0.3cm³/g and microcrystal more than at least 400m²/g improves sharply rather than the other thing in at least 0.70 or more things. By these, as a graphite system hydrogen absorption ingredient, though a raw material graphite is ground and activation processed, it becomes the most desirable mode that the magnitude of the microcrystal after that the magnitude of the microcrystal of a raw material graphite makes it 25nm or more in a field (011), and makes it 20nm or more in a field (002) and grinding adjusts to 1nm or more in a field (011), and adjusts to the range of 1-70nm ** in a field (002).

[0022] (Examples 8-12) This example is a thing when investigating the effectiveness when containing Pt, Pd, nickel, K, and Li in a graphite, and Pt support, Pd support, and preparation of nickel support graphite are the examples which used the sample after activation processing of the above-mentioned example 1. the content approach -- H₂ -- after dissolving PtCl₆, PdCl₂, or nickel (NO₃)₂ in pure water, the sample after activation processing of an example 1 is supplied, and it fully mixes, and it was made to sink in and was made to dry Then, hydrogen reduction was carried out at 400 degrees C, and the graphite floc front face was made to distribute Pt, Pd, or nickel. After paying and carrying out the vacuum deairing of the sample after activation processing of an example 1 into a stainless steel container about distribution of K and Li, about 280 degrees C and Li, the temperature up was carried out [K] to 420 degrees C, and each sample graphite was made to distribute K or Li. The content element, the amount (mass %) of distributions (content), and its evaluation result of each [these] sample were shown in Table 3. Table 3 shows that all the examples 8-12 of a cycle property [a hydrogen storage capacity and] can improve from the sample configuration of an example 1. In the thing of the example 8 which contained Pt especially, it increases to about about 1.6 times with the hydrogen storage capacity after repeating 1.8 times, a cycle property, i.e., occlusion, and emission 5 times with a hydrogen storage capacity, and an improvement effect is remarkable.

[0023]

[Table 3]

[0024]

[Effect of the Invention] As mentioned above, using the crystalline high graphite with easy acquisition and manufacture as a raw material, the graphite system hydrogen absorption ingredient and its manufacture approach of invention are adjusting to a predetermined specification value combining grinding and activation processing, and can likeness[easy]-attain high hydrogen absorption nature physically and chemically. Thereby, the occlusion of a lot of hydrogen can be carried out efficiently, and when it can be used repeatedly, it can be lightweight, and this invention is easy also for the manufacture approach, it holds down a manufacturing cost and can be contributed to utilization.

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